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(54)【発明の名称】 低温活性に優れた三元触媒の製造方法

(57)【要約】

【目的】 三元触媒で排ガス温度が低い条件でも十分な
浄化活性を示すようにする。

【構成】 pHを10より大きく調整した貴金属塩水溶
液を、ペロブスカイト型複合酸化物担体または更に耐熱
性酸化物を含んだ担体に含浸させ、乾燥後、焼成する。

【特許請求の範囲】

【請求項1】 pHを10より大きく調整した貴金属塩水溶液を担体に含浸させ、乾燥後、焼成することを特徴とする触媒の製造方法。

【請求項2】 貴金属はPd, Pt, Ru, Rh及びIrからなる群より選ばれた1種又は2種以上の金属である請求項1、2又は3に記載の触媒の製造方法。

【請求項3】 貴金属はPdである請求項4に記載の触媒の製造方法。

【請求項4】 担体が一般式 $L_{n-x}AxMO_x$ (L_n はCeを除く希土類金属、AはCe又はアルカリ土類金属、MはMn, Fe, Co, Ni, Cu, Pd及びRuからなる遷移金属で、いずれも1種又は2種以上、 $0 < x < 1$) で示されるペロブスカイト型構造の複合酸化物である請求項1に記載の触媒の製造方法。

【請求項5】 Ce及びZr、又はさらにCe以外の希土類金属を含み少なくとも一部が複合酸化物又は固溶体となっている耐熱性酸化物を助触媒さらに含ませる請求項4に記載の触媒の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は一酸化炭素(CO)、炭化水素(HC)及び酸化窒素(NO_x)の浄化能力に優れた排気ガス浄化用三元触媒、特に自動車用ガソリンエンジンなどにおいて、アイドリング時などの排ガス温度が低い条件でも浄化活性を示す三元触媒と、その製造方法に関するものである。

【0002】

【従来の技術】 排気ガス浄化用三元触媒としてはアルミニナ単体にPt, Rh, Pdなどの貴金属を担持した貴金属触媒が実用化されて広く使用されている。また、希土類金属、アルカリ土類金属及び遷移金属から構成されるペロブスカイト型構造を有する複合酸化物は、CO、HC及びNO_xを浄化する安価な排気ガス浄化用三元触媒として実用化が期待されている(特開昭59-87046号公報、特開昭60-82138号公報参照)。このペロブスカイト型複合酸化物はCO、HCの浄化能力は優れているが、NO_xの浄化能力がやや劣っており、自動車排ガス用の三元触媒として実用に供するには十分でない。そこで、ペロブスカイト型複合酸化物触媒のNO_x浄化能力を高めるために、貴金属を共存させることも提案されている(特開平1-168343号公報、特開平2-90947号公報参照)。特に特開平2-90947号公報にはpHを7~10に調整した貴金属塩水溶液をペロブスカイト型複合酸化物担体に含浸させ、乾燥後、焼成する方法が記載されている。

【0003】

【発明が解決しようとする課題】 これらの触媒は、自動車のガソリンエンジンにおいて、走行時のような排ガス温度が高い条件では優れた浄化活性を示すが、アイドリ

ング時などの排ガス温度が低い条件では十分な浄化活性を示さない。排ガス規制強化とともにこのような排ガス温度が低い条件でも十分な浄化活性を示す触媒が望まれている。本発明は排ガス温度が低い条件でも十分な浄化活性を示す三元触媒を製造する方法を提供することを目的とするものである。

【0004】

【課題を解決するための手段】 本発明では、pHを10より大きく調整した貴金属塩水溶液を担体に含浸させ、乾燥後、焼成する。貴金属はPd, Pt, Ru, Rh及びIrからなる群より選ばれた1種又は2種以上の金属であり、特にPdが好ましい。担体は、Al₂O₃、又は一般式 $L_{n-x}AxMO_x$ (L_n はCeを除く希土類金属、AはCe又はアルカリ土類金属、MはMn, Fe, Co, Ni, Cu, Pd及びRuからなる遷移金属で、いずれも1種又は2種以上、 $0 < x < 1$) で示されるペロブスカイト型構造の複合酸化物である。

【0005】 この触媒で高温においても浄化活性を維持できるようにするためには、Ce及びZr、又はさらにCe以外の希土類金属を含み少なくとも一部が複合酸化物又は固溶体となっている耐熱性酸化物を助触媒としてさらに含ませる。担体100重量部に対して、貴金属換算で0.2~5.0重量部を含みpHが10より大きく調整された貴金属塩水溶液を含浸させ、乾燥後250~800°Cの温度で焼成する。

【0006】 水溶性貴金属塩としては、テトラアミンバラジウムジクロライドPd(NH₃)₄C₁、やテトラアミンバラジウム水酸塩Pd(NH₃)₄(OH)₂などの塩基性水溶液にアンモニア水や酸を添加してpH>10になるように調製して用いるか、PdCl₂、PtCl₂、RuCl₃·3H₂Oなどの塩化物、Pd(NO₃)₂、Ru(NO₃)₃、Rh(NO₃)₃などの硝酸塩、又はPd(NO₂)₂(NH₃)₂などのジニトロジアミン塩などの酸性水溶液にアンモニア水を添加してpH>10になるように調製して用いる。

【0007】

【発明の効果】 本発明の方法により製造される触媒はアイドリング時などの排ガス温度が百数十~二百数十°Cの低い条件においても浄化活性を示すことができる。また、耐熱性酸化物をさらに含めた場合には、900°C以上の高温でも耐久性のある触媒となる。

【0008】

【実施例】

(実施例1) 硝酸バラジウム溶液(Pd分4.4重量%) 25重量部を純水1700重量部で希釈した。Pd換算で1.1重量部となった。この溶液はpHが1.7であったので、アンモニア水を添加してpHが11.0となるように溶液を調製した。担体に用いるペロブスカイト型複合酸化物と耐熱性酸化物は次のように作成した。ペロブスカイト型複合酸化物を共沈法により作成するた

めに、硝酸ランタン 103.9 g、硝酸セリウム 26.1 g、硝酸コバルト 34.9 g、硝酸鉄 72.7 g を純水に溶解した水溶液 0.3 リットルと、中和共沈剤としての炭酸ナトリウム 50 g を溶解した水溶液 0.5 リットルとを用意し、中和共沈剤を先の水溶液に滴下し、共沈物を得た。その共沈物を十分水洗し、濾過した後、真空乾燥した。これを 600°C で 3 時間大気中で焼成後、粉碎し、その後、800°C で 3 時間大気中で焼成を行ない、さらに粉碎してペロブスカイト型複合酸化物 ($\text{La}_{0.1}\text{Ce}_{0.1}(\text{Co}_{0.4}\text{Fe}_{0.4})\text{O}_3$) の粉末を作成した。耐熱性酸化物を作成するため、市販の高比表面積の酸化セリウム粉末 (CeO_2 比表面積 170 m^2/g 、純度 99.9% / TREO (全希土類酸化物)) 111.9 g を用意し、これにオキシ硝酸ジルコニウム ($\text{ZrO}(\text{NO}_3)_2$) 水溶液 (液比重 1.51、液中に ZrO_2 換算で 25.0 重量% 含まれる) 147.9 g、及び硝酸イットリウム ($\text{Y}(\text{NO}_3)_3$) 水溶液 (液比重 1.62、液中に Y_2O_3 換算で 21.7 重量% 含まれる) 26.0 g を加え、よく攪拌して混合しながら 110°C で 10 時間大気中で乾燥した。その後、大気中で 600°C で 3 時間焼成を行ない、($\text{Ce}_{0.1}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_3$) 複合酸化物を約 15.0 g 得た。

【0009】スラリーコート担体を得るために、先のペロブスカイト型複合酸化物 ($\text{La}_{0.1}\text{Ce}_{0.1}(\text{Co}_{0.4}\text{Fe}_{0.4})\text{O}_3$) の 50 重量部と、耐熱性酸化物 ($\text{Ce}_{0.1}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_3$) の 50 重量部とを純水 100 重量部に加え、ボールミルで 12 時間粉碎して得たスラリーをコーチェライト質の耐熱性ハニカム担体に流し込み、余部のスラリーを空気流で吹き払い、乾燥 (例えば 130°C で 24 時間) させた後、600°C で大気中 3 時間焼成してペロブスカイト型複合酸化物と耐熱性酸化物が均一にコーティングされた担体を得た。上記パラジウム塩水溶液 ($\text{pH} = 11.0$) を 40°C に保温し、それに上記のコーティング担体を含浸させて 2 時間保持し、パラジウムを吸着させた。それを 130°C で 24 時間乾燥し、大気中で 600°C で 3 時間焼成して実施例 1 の試料を得た。

【0010】(実施例 2) 硝酸パラジウム溶液 (Pd 分 4.4 重量%) 40 重量部を純水 1700 重量部で希釈して、Pd 換算で 1.76 重量部、 pH が 1.4 の溶液を得、これにアンモニア水を添加して pH が 10.7 となるように溶液を調製した。担体は、中和共沈法により作成したペロブスカイト型複合酸化物 ($\text{La}_{0.1}\text{Sr}_{0.1}(\text{Co}_{0.4}\text{Fe}_{0.4})\text{O}_3$) の 50 重量部と、酸化セリウムにジルコニアを固溶させた耐熱性酸化物 ($\text{Ce}_{0.1}\text{Zr}_{0.1}\text{O}_3$) の 20 重量部とを用いて、実施例 1 と同様にしてコーチェライト質の耐熱性ハニカム担体にペロブスカイト型複合酸化物と耐熱性酸化物が均一にコーティングされた担体を得た。この担体を上記のパラジウム塩水溶液 ($\text{pH} = 10.7$) に含浸させ、実施例 1 と同様にしてパラジウムを吸着させ、乾燥後、大気中で 250°C で 3

時間焼成して実施例 2 の試料を得た。

【0011】(実施例 3) テトラアミンパラジウム硝酸塩水溶液 (Pd 分 4.6 重量% 溶液で、 $\text{pH} = 8.5$) 23.9 重量部 (Pd 換算で 0.5 重量部) に純水 100 重量部を加え、アンモニア水を添加して pH が 11.2 となるように溶液を調製した。担体は、ペロブスカイト型複合酸化物 ($\text{La}_{0.1}\text{Sr}_{0.1}(\text{Co}_{0.4}\text{Fe}_{0.4})\text{O}_3$) の 50 重量部と、市販の SrZrO_3 の 50 重量部とを用いて、実施例 1 と同様にしてコーチェライト質の耐熱性ハニカム担体にペロブスカイト型複合酸化物と耐熱性酸化物が均一にコーティングされた担体を得た。この担体に上記のパラジウム塩水溶液 ($\text{pH} = 11.2$) の全量を含浸させ、乾燥後、大気中で 600°C で 3 時間焼成して実施例 3 の試料を得た。

【0012】(実施例 4) テトラアミンパラジウムジクロライド水溶液 (Pd 分 8.4 重量% で、 $\text{pH} = 8.7$) 13 重量部にアンモニア水を加え、イオン交換して塩素イオンを取り除き、 pH が 12.0 の水溶液 12.7 重量部を得た。実施例 1 で用いたのと同じコーティング担体を用意し、その担体に上記のパラジウム塩水溶液 ($\text{pH} = 12.0$) の全量を含浸させ、乾燥後、大気中で 250°C で 3 時間焼成して実施例 4 の試料を得た。

【0013】(実施例 5) テトラアミンパラジウム硝酸塩水溶液 (Pd 分 4.6 重量%) 23.9 重量部 (Pd 換算で 0.5 重量部) に純水 100 重量部を加え、アンモニア水を添加して pH が 12.0 となるように溶液を調製した。担体は中和共沈法により作成したペロブスカイト型複合酸化物 ($\text{La}_{0.1}\text{Ce}_{0.1}(\text{Co}_{0.4}\text{Fe}_{0.4})\text{O}_3$) の 50 重量部と実施例 1 で用意した ($\text{Ce}_{0.1}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_3$) を用いて、実施例 1 と同様にしてコーチェライト質の耐熱性ハニカム担体にペロブスカイト型複合酸化物と耐熱性酸化物が均一にコーティングされた担体を得た。この担体に上記のパラジウム塩水溶液 ($\text{pH} = 12.0$) の全量を含浸させ、乾燥後、大気中 250°C で 3 時間焼成して実施例 5 の試料を得た。

【0014】(実施例 6) ヘキサンミンテラクロライド白金水溶液 (Pt 分 1.45 重量%) 34.5 重量部 (Pt 換算で 0.5 重量部) に純水 100 重量部を加え、アンモニア水を添加して pH が 11.3 となるように溶液を調製した。担体はペロブスカイト型複合酸化物 ($\text{La}_{0.1}\text{Sr}_{0.1}(\text{Co}_{0.4}\text{Fe}_{0.4})\text{O}_3$) の 80 重量部と市販の SrZrO_3 の 20 重量部とを用いて、実施例 1 と同様にしてコーチェライト質の耐熱性ハニカム担体にペロブスカイト型複合酸化物と耐熱性酸化物が均一にコーティングされた担体を得た。この担体に上記の白金塩水溶液 ($\text{pH} = 11.3$) の全量を含浸させ、乾燥後、大気中 600°C で 3 時間焼成して実施例 6 の試料を得た。

【0015】(比較例 a) 硝酸パラジウム水溶液にアンモニア水を添加して pH を 6.9 に調整した点を除いて、実施例 1 と同様にして比較例 a の試料を得た。

(比較例b) 硝酸パラジウム水溶液にアンモニア水を添加してpHを8.5に調整した点を除いて、実施例1と同様にして比較例bの試料を得た。

(比較例c) 硝酸パラジウム水溶液にアンモニア水を添加してpHを9.7に調整した点を除いて、実施例1と同様にして比較例cの試料を得た。

【0016】(比較例d) 硝酸パラジウム溶液25重量部を純水100重量部で希釈してpHが1.7の水溶液を得た。担体はペロブスカイト型複合酸化物($\text{La}_{0.8}\text{Sr}_{0.2}(\text{Co}_{0.4}\text{Fe}_{0.6})\text{O}_3$)の50重量部と市販の SrZrO_3 *10

* ZrO_3 の50重量部とを用いて作成した実施例3と同じコーティング担体を用いた。他の条件は実施例1と同様にして比較例dの試料を得た。

(比較例e) 広く実用化されている自動車用三元触媒である $\text{Pt-Rh}/\gamma-\text{Al}_2\text{O}_3$ 触媒を比較例eとした。Pt-Rhの含有量は0.43重量部であった。これらの結果を表1にまとめて示す。

【0017】

【表1】

No	出発系 []の数値は重量部		貴金属	溶液	pH	焼成
	ペロブスカイト型酸化物	耐熱酸化物				
1	[50] ($\text{La}_{0.8}\text{Ce}_{0.2}$) ($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3	[50] ($\text{Ce}_{0.65}\text{Zr}_{0.3}\text{Y}_{0.05}$) O_2	[1.1] Pd	11.0	600°C	
2	[80] ($\text{La}_{0.8}\text{Sr}_{0.2}$) ($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3	[20] ($\text{Ce}_{0.8}\text{Zr}_{0.2}$) O_2	[1.76] Pd	10.7	250°C	
3	[50] ($\text{La}_{0.8}\text{Sr}_{0.2}$) ($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3	[50] SrZrO_3	[0.5] Pd	11.2	600°C	
4	[50] ($\text{La}_{0.8}\text{Ce}_{0.2}$) ($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3	[50] ($\text{Ce}_{0.65}\text{Zr}_{0.3}\text{Y}_{0.05}$) O_2	[1.1] Pd	12.0	250°C	
5	[50] ($\text{La}_{0.9}\text{Ce}_{0.1}$) ($\text{Co}_{0.38}\text{Fe}_{0.58}\text{Ru}_{0.08}$) O_3	[50] ($\text{Ce}_{0.65}\text{Zr}_{0.3}\text{Y}_{0.05}$) O_2	[0.6] Pd	12.0	250°C	
6	[80] ($\text{La}_{0.8}\text{Sr}_{0.2}$) ($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3	[20] SrZrO_3	[0.6] Pt	11.3	600°C	
a	[50] ($\text{La}_{0.8}\text{Ce}_{0.2}$) ($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3	[50] ($\text{Ce}_{0.65}\text{Zr}_{0.3}\text{Y}_{0.05}$) O_2	[1.1] Pd	6.9	600°C	
b	[50] ($\text{La}_{0.8}\text{Ce}_{0.2}$) ($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3	[50] ($\text{Ce}_{0.65}\text{Zr}_{0.3}\text{Y}_{0.05}$) O_2	[1.1] Pd	8.5	600°C	
c	[50] ($\text{La}_{0.8}\text{Ce}_{0.2}$) ($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3	[50] ($\text{Ce}_{0.65}\text{Zr}_{0.3}\text{Y}_{0.05}$) O_2	[1.1] Pd	9.7	600°C	
d	[50] ($\text{La}_{0.8}\text{Sr}_{0.2}$) ($\text{Co}_{0.4}\text{Fe}_{0.6}$) O_3	[50] SrZrO_3	[1.1] Pd	1.7	600°C	
e		[100] $\gamma\text{-Al}_2\text{O}_3$	[0.43] Pt-Rh	1.8	250°C	

【0018】これらの実施例の試料と比較例の試料を用いて、以下の条件で触媒活性を測定と耐久試験を行なった。

触媒活性の測定

ハニカム状(セル数300/inch²)コーチェライト担体に担持されたそれぞれの試料(直径30mm、長さ50mm)を下記のモデルガスにて活性を測定した。ガス※

※温度は触媒への入口ガス温度で示し、室温から昇温し、 NO 、 CO 、 HC (C_1 換算濃度)のそれぞれが初期濃度の50%に低下した温度を50%浄化温度とする。

40 また、リッチガスとリーンガスはそれぞれ1秒毎に切り換えた。触媒を通るガス流の空間速度(SV)は30,000/時間とした。

【0019】

	リッチガス	リーンガス
CO	2.6 %	0.7 %
HC(C_1 換算濃度)	0.19%	0.19%
H_2	0.87%	0.23%
CO_2	8 %	8 %
NO	0.17%	0.17%
O_2	0.65%	1.8 %

7
 H_2O 10% 10%
 N₂ 残部 残部

【0020】耐久試験

上記のリッチガスとリーンガスを5秒毎に切り換えて9

* 定結果と耐久試験後の触媒活性の試験結果を表2に示す。

00°Cで30分、750°Cで30分のサイクルを15回

【0021】

繰り返して耐久試験を行なった。耐久試験後にも前記の

【表2】

方法で触媒活性を測定した。耐久試験前の触媒活性の測*

各試験での50%浄化温度(°C)

No.	初期			耐久後		
	NO	CO	HC	NO	CO	HC
実施例 1	207	204	215	268	274	287
実施例 2	140	150	151	221	218	233
実施例 3	215	217	223	271	266	278
実施例 4	136	132	138	207	227	228
実施例 5	156	141	155	211	227	232
実施例 6	186	158	158	260	225	257
比較例 a	236	227	242	370	332	349
比較例 b	253	245	256	374	288	332
比較例 c	233	225	236	432	365	382
比較例 d	317	306	341	>500	394	393
比較例 e	198	193	208	259	263	276

【0022】表1の結果から明らかなように、各実施例 30 では50%浄化温度が低く、各比較例では高い。

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TANAKA HIROHISA

(54) PRODUCTION OF TERNARY CATALYST EXCELLENT IN LOW-TEMPERATURE ACTIVITY

(57)Abstract:

PURPOSE: To obtain the ternary catalyst capable of sufficiently purifying even a low-temp, exhaust gas by impregnating a perovskite-structure multiple oxide carrier or further a carrier contg. a heat-resistant oxide with an aq. soln. of noble metal salts with the pH specified, drying and then calcining the impregnated carrier.

CONSTITUTION: A carrier is impregnated with an aq. soln. of noble metal salts adjusted to \geq pH10, and the impregnated carrier is dried and then calcined. One or \geq 2 kinds of metals are selected from the group consisting of Pd, Pt, Ru, Rh and Ir and used as the noble metals, and Pd is especially preferable. The carrier is the perovskite-structure multiple oxide expressed by the formula $Ln_{1-x}AxMo_3$ (Ln is the rare-earth metals except Cl, A is Cl or alkaline-earth metals, M is one or \geq 2 kinds among the transition metals consisting of Mn, iron, Co, Ni, Cu, Pd and Ru and $0 < x < 1$). Meanwhile, a heat-resistant oxide contg. Cl, Zn and rare-earth metals other than Ce and at least a part of which forms a multiple oxide is further incorporated as a promoter.

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JAPANESE [JP,05-220395,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS
EXAMPLE

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the catalyst characterized by infiltrating support and calcinating after desiccation the noble-metals salt water solution which adjusted pH more greatly than 10.

[Claim 2] Noble metals are the manufacture approaches of the catalyst according to claim 1, 2, or 3 which are one sort or two sorts or more of metals chosen from the group which consists of Pd, Pt, Ru, Rh, and Ir.

[Claim 3] Noble metals are the manufacture approaches of the catalyst according to claim 4 which is Pd.

[Claim 4] The manufacture approach of the catalyst according to claim 1 which is the multiple oxide of perovskite type structure in which support is shown by general formula $Ln_{1-x}AxMO_3$ (the rare earth metal except Ce and A are the transition metals which consist of Mn, Fe, Co, nickel, Cu, Pd, and Ru, and Ln is [Ce or alkaline earth metal, and M] all one sort or two sorts or more, and $0 < x < 1$).

[Claim 5] The manufacture approach of a catalyst according to claim 4 of including Ce and Zr, or the heat-resistant oxide with which at least the part serves as a multiple oxide or the solid solution including rare earth metals other than Ce further in a co-catalyst pan.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the three way component catalyst which shows purification activity also on the conditions that the exhaust gas temperature at the time of an idling etc. is low, and its manufacture approach in the three way component catalyst for exhaust gas purification excellent in the purification capacity of a carbon monoxide (CO), a hydrocarbon (HC), and nitrogen oxide (NOx), especially the gasoline engine for automobiles, etc.

[0002]

[Description of the Prior Art] As a three way component catalyst for exhaust gas purification, the precious metal catalyst which supported noble metals, such as Pt, Rh, and Pd, is put in practical use by the alumina simple substance, and it is widely used for it. Moreover, utilization is expected as a cheap three way component catalyst for exhaust gas purification with which the multiple oxide which has the perovskite type structure which consists of a rare earth metal, an alkaline earth metal, and transition metals purifies CO, HC, and NOx (refer to JP,59-87046,A and JP,60-82138,A). Although CO and the purification capacity of HC are excellent, this perovskite mold multiple oxide is a little inferior in the purification capacity of NOx, and they are not enough to present practical use as a three way component catalyst for automobile exhaust. Then, in order to heighten the NOx purification capacity of a perovskite mold multiple oxide catalyst, also making noble metals live together is proposed (refer to JP,1-168343,A and JP,2-90947,A). The noble-metals salt water solution which adjusted pH to 7-10 is infiltrated into perovskite mold multiple oxide support, and the approach of calcinating is indicated by especially JP,2-90947,A after desiccation.

[0003]

[Problem(s) to be Solved by the Invention] In the gasoline engine of an automobile, although these catalysts show the purification activity excellent in the conditions that exhaust gas temperature like [at the time of transit] is high, they do not show purification activity sufficient on the conditions that the exhaust gas temperature at the time of an idling etc. is low. A catalyst which shows sufficient purification activity also on the conditions that such exhaust gas temperature is low, with exhaust gas toughening of regulations is desired. This invention aims at offering the approach of manufacturing the three way component catalyst which shows purification activity sufficient also on the conditions that exhaust gas temperature is low.

[0004]

[Means for Solving the Problem] In this invention, support is infiltrated and the noble-metals salt water solution which adjusted pH more greatly than 10 is calcinated after desiccation. Noble metals are one sort or two sorts or more of metals chosen from the group which consists of Pd, Pt, Ru, Rh, and Ir, and especially its Pd is desirable. Support is the multiple oxide of the perovskite type structure shown by aluminum 2O3 or general formula Ln_{1-x}A_xMO₃ (the rare earth metal except Ce and A are the transition metals which consist of Mn, Fe, Co, nickel, Cu, Pd, and Ru, and Ln is [Ce or alkaline earth metal, and M] all one sort or two sorts or more, and 0<x<1).

[0005] In order to enable it to maintain purification activity also in an elevated temperature with this catalyst, Ce and Zr, or the heat-resistant oxide with which at least the part serves as a multiple oxide or the solid solution including rare earth metals other than Ce further is further included as a co-catalyst. The noble-metals salt water solution with which pH was adjusted including the 0.2 - 5.0 weight section more greatly than 10 by noble-metals conversion is infiltrated to the support 100 weight section, and it calcinates at the temperature of 250-800 degrees C after desiccation.

[0006] as a water-soluble noble-metals salt — tetra — amine palladium dichloride Pd(NH₃)₄Cl₂ — tetra — whether it prepares and uses so that aqueous ammonia and an acid may be added in basic water solutions, such as amine palladium oxalate Pd(NH₃)₄(OH)₂, and it may be set to pH>10 Nitrates, such as chlorides, such as PdCl₂, PtCl₂, and RuCl₃·3H₂O, and Pd (NO₃)₂, Ru (NO₃)₃, Rh (NO₃)₃. Or it prepares and uses so that aqueous ammonia may be added to aqueous acids, such as dinitro diamine salts, such as Pd(NO₂)₂(NH₃)₂ and Pt(NO₂)₂(NH₃)₂, and it may be set to pH>10.

[0007]

[Effect of the Invention] the catalyst manufactured by the approach of this invention — the exhaust gas temperature at the time of an idling etc. — 100 — dozens-200 — purification activity can be shown also in the low conditions which are dozens of degrees C. Moreover, when a heat-resistant oxide is included further, even an elevated temperature 900 degrees C or more serves as a durable catalyst.

[0008]

[Example]

(Example 1) The palladium nitrate solution (Pd 4.4 % of the weight per part) 25 weight section was diluted with the pure-water 1700 weight section. It became the 1.1 weight section by Pd conversion. Since pH was 1.7, this solution prepared the solution so that aqueous ammonia might be added and pH might be set to 11.0. The perovskite mold multiple oxide and the heat-resistant oxide which are used for support were created as follows. In order to create a perovskite mold multiple oxide with a coprecipitation method, 103.9g of lanthanum nitrates, 26.1g of cerium nitrates, 34.9g of cobalt nitrates, 0.3l. of water solutions which dissolved 72.7g of iron nitrate in

pure water, and 0.5l. of water solutions which dissolved 50g of sodium carbonates as a neutralization coprecipitator were prepared, the neutralization coprecipitator was dropped at the previous water solution, and the coprecipitate was obtained. The vacuum drying was carried out, after rinsing the coprecipitate enough and filtering it. This was ground after baking in 3-hour atmospheric air at 600 degrees C, and it calcinated in 3-hour atmospheric air at 800 degrees C after that, it ground further, and the powder of the perovskite mold multiple oxide (La0.8Ce0.2₂ (Co0.4Fe0.6)O₃ was created. In order to create a heat-resistant oxide Commercial cerium oxide powder of high specific surface area (2/g CeO₂ specific surface area of 170m) 99.9% of purity and TREO(all rare earth oxides) 111.9g are prepared. To this, 147.9g (contained 25.0% of the weight by ZrO₂ conversion in liquid density 1.51 and liquid) of oxy-zirconium-nitrate (ZrO₂ (NO₃)) water solutions, And 26.0g (contained 21.7% of the weight by 2YO₃ conversion in liquid density 1.62 and liquid) of nitric-acid yttrium (Y(NO₃)₃) water solutions was added, and it dried in 10-hour atmospheric air at 110 degrees C, having agitated well and mixing. Then, baking was performed at 600 degrees C in atmospheric air for 3 hours, and about 150g of O(Ce0.65Zr0.30Y0.05)₂ multiple oxides was obtained.

[0009] In order to obtain slurry coat support, they are 50 weight sections of the previous perovskite mold multiple oxide (La0.8Ce0.2) (Co0.4Fe0.6)O₃, 50 weight sections of the heat-resistant oxide (Ce0.65Zr0.30Y0.05)O₂ were added to the pure-water 100 weight section, the slurry which ground for 12 hours and was obtained with the ball mill was slushed into the heat-resistant honeycomb support of the quality of cordierite, and after blowing off and drying the slurry of the complementary section by airstream (it is 24 hours at 130 degrees C), the support which is calcinated among atmospheric air at 600 degrees C for 3 hours and by which coating of a perovskite mold multiple oxide and the heat-resistant oxide was carried out to homogeneity was obtained. The above-mentioned palladium salt water solution (pH=11.0) was kept warm at 40 degrees C, and the above-mentioned coating support was infiltrated into it, it held for 2 hours, and palladium was made to adsorb. It was dried at 130 degrees C for 24 hours, it calcinated at 600 degrees C in atmospheric air for 3 hours, and the sample of an example 1 was obtained.

[0010] (Example 2) The palladium nitrate solution (Pd 4.4 % of the weight per part) 40 weight section was diluted with the pure-water 1700 weight section, and the 1.76 weight section and pH obtained the solution of 1.4 by Pd conversion, and the solution was prepared so that aqueous ammonia might be added to this and pH might be set to 10.7. Support obtained the support by which coating of a perovskite mold multiple oxide and the heat-resistant oxide was carried out to the heat-resistant honeycomb support of the quality of cordierite like the example 1 at homogeneity using 50 weight sections of the perovskite mold multiple oxide (La0.8Sr0.2) (Co0.4Fe0.6)O₃ created with the neutralization coprecipitation method, and 20 weight sections of the heat-resistant oxide (Ce0.8Zr0.2)O₂ which made the zirconia dissolve to cerium oxide. Infiltrate this support into the above-mentioned palladium salt water solution (pH=10.7), and palladium was made to adsorb like an example 1, after desiccation, it calcinated at 250 degrees C in atmospheric air for 3 hours, and the sample of an example 2 was obtained.

[0011] (Example 3) The pure-water 100 weight section was added to the tetra-amine palladium nitrate water-solution (with Pd 4.6-% of the weight solution per part, it is pH=8.5) 23.9 weight section (it is the 0.5 weight section by Pd conversion), and the solution was prepared so that aqueous ammonia might be added and pH might be set to 11.2. Support obtained the support by which coating of a perovskite mold multiple oxide and the heat-resistant oxide was carried out to the heat-resistant honeycomb support of the quality of cordierite like the example 1 at homogeneity using 50 weight sections of the perovskite mold multiple oxide (La0.8Sr0.2) (Co0.4Fe0.6)O₃, and 50 commercial weight sections of SrZrO₃. The whole quantity of the above-mentioned palladium salt water solution (pH=11.2) was infiltrated into this support, after desiccation, it calcinated at 600 degrees C in atmospheric air for 3 hours, and the sample of an example 3 was obtained.

[0012] (Example 4) The ion exchange of the aqueous ammonia was added and carried out to the tetra-amine palladium dichloride water-solution (Pd 8.4 % of the weight per part, pH= 8.7) 13 weight section, the chlorine ion was removed, and pH obtained the water-solution 127 weight section of 12.0. The same coating support as having used in the example 1 is prepared, the whole quantity of the above-mentioned palladium salt water solution (pH=12.0) was infiltrated into the support, after desiccation, it calcinated at 250 degrees C in atmospheric air for 3 hours, and the sample of an example 4 was obtained.

[0013] (Example 5) The pure-water 100 weight section was added to the tetra-amine palladium nitrate water-solution (Pd 4.6 % of the weight per part) 23.9 weight section (it is the 0.5 weight section by Pd conversion), and the solution was prepared so that aqueous ammonia might be added and pH might be set to 12.0. Support obtained the support by which coating of a perovskite mold multiple oxide and the heat-resistant oxide was carried out to the heat-resistant honeycomb support of the quality of cordierite like the example 1 at homogeneity using O(Ce0.65Zr0.30Y0.05)₂ prepared in 50 weight sections and the example 1 of the perovskite mold multiple oxide (La0.9Ce0.1) (Co0.38Fe0.56Ru0.06)O₃ created with the neutralization coprecipitation method. The whole quantity of the above-mentioned palladium salt water solution (pH=12.0) was infiltrated into this support, it calcinated at 250 degrees C after desiccation and among atmospheric air for 3 hours, and the sample of an example 5 was obtained.

[0014] (Example 6) The pure-water 100 weight section was added to the hexa ammine tetra-chloride platinum water-solution (Pt 1.45 % of the weight per part) 34.5 weight section (it is the 0.5 weight section by Pt conversion), and the solution was prepared so that aqueous ammonia might be added and pH might be set to 11.3. Support obtained the support by which coating of a perovskite mold multiple oxide and the heat-resistant oxide was carried out to the heat-resistant honeycomb support of the quality of cordierite like the example 1 at homogeneity using the perovskite mold multiple oxide (La0.8Sr0.2) (Co0.4Fe0.6)O₃ 380 weight section and the commercial SrZrO₃ 20 weight section. The whole quantity of the above-mentioned platinum-salts water solution (pH=11.3) was infiltrated into this support, it calcinated at 600 degrees C after desiccation and among atmospheric air for 3 hours, and the sample of an example 6 was obtained.

[0015] ((a) The example of a comparison) Except for the point of having added aqueous ammonia in the palladium nitrate water solution, and having adjusted pH to 6.9, the sample of the example a of a comparison was obtained like the example 1.

((b) The example of a comparison) Except for the point of having added aqueous ammonia in the palladium nitrate water solution, and having adjusted pH to 8.5, the sample of the example b of a comparison was obtained like the example 1.

((c) The example of a comparison) Except for the point of having added aqueous ammonia in the palladium nitrate water solution, and having adjusted pH to 9.7, the sample of the example c of a comparison was obtained like the example 1.

[0016] ((d) The example of a comparison) The palladium nitrate solution 25 weight section was diluted with the pure-water 100 weight section, and pH obtained the water solution of 1.7. Support used the same coating support as the example 3 created using 50 weight sections of the perovskite mold multiple oxide (La0.8Sr0.2) (Co0.4Fe0.6) O₃, and 50 commercial weight sections of SrZrO₃. Other conditions obtained the sample of the example d of a comparison like the example 1.

((e) The example of a comparison) 20Pt-Rh/gamma-aluminum 3 catalyst which is a three way component catalyst for automobiles put in practical use widely was made into the example e of a comparison. The content of Pt-Rh was the 0.43 weight section. These results are collectively shown in Table 1.

[0017]

[Table 1]

No	出発系 []の数値は重量部		貴金属	溶液	pH	焼成
	ペロブスカイト型酸化物	耐熱酸化物				
1	[50](La _{0.8} Co _{0.2}) (Co _{0.4} Fe _{0.6}) O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05}) O ₂	[1.1]Pd	11.0	600℃	
2	[80](La _{0.8} Si _{0.2}) (Co _{0.4} Fe _{0.6}) O ₃	[20](Ce _{0.65} Zr _{0.3}) O ₂	[1.76]Pd	10.7	250℃	
3	[50](La _{0.8} Si _{0.2}) (Co _{0.4} Fe _{0.6}) O ₃	[50]SrZrO ₃	[0.5]Pd	11.2	600℃	
4	[50](La _{0.8} Co _{0.2}) (Co _{0.4} Fe _{0.6}) O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05}) O ₂	[1.1]Pd	12.0	250℃	
5	[50](La _{0.9} Co _{0.1}) (Co _{0.38} Fe _{0.58} Ru _{0.08}) O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05}) O ₂	[0.6]Pd	12.0	250℃	
6	[80](La _{0.8} Si _{0.2}) (Co _{0.4} Fe _{0.6}) O ₃	[20]SrZrO ₃	[0.6]Pt	11.3	600℃	
a	[50](La _{0.8} Co _{0.2}) (Co _{0.4} Fe _{0.6}) O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05}) O ₂	[1.1]Pd	6.9	600℃	
b	[50](La _{0.8} Co _{0.2}) (Co _{0.4} Fe _{0.6}) O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05}) O ₂	[1.1]Pd	8.5	600℃	
c	[50](La _{0.8} Co _{0.2}) (Co _{0.4} Fe _{0.6}) O ₃	[50](Ce _{0.65} Zr _{0.3} Y _{0.05}) O ₂	[1.1]Pd	9.7	600℃	
d	[50](La _{0.8} Si _{0.2}) (Co _{0.4} Fe _{0.6}) O ₃	[50]SrZrO ₃	[1.1]Pd	1.7	600℃	
e		[100]γ-Al ₂ O ₃	[0.43]	1.8	250℃	
			Pt-Rh			

[0018] Measurement and a durability test were performed for catalytic activity on condition that the following using the sample of these examples, and the sample of the example of a comparison.

Activity was measured for each sample (the diameter of 30mm, die length of 50mm) supported by the measurement honeycomb-like (number of cels 300-/inch²) cordierite support of catalytic activity by the following model gas. The inlet gas temperature to a catalyst shows gas temperature, it carries out a temperature up from a room temperature, and makes purification temperature temperature to which each of NO, CO, and HC (C₃H₆+C₃H₈) fell to 50% of initial concentration 50%. Moreover, rich gas and lean gas were switched for every second, respectively. Space velocity (SV) of the gas stream which passes along a catalyst was made into 30,000-/time amount.

[0019]

Rich gas Lean gas CO 2.6 % 0.7 % HC (C₁ conversion concentration) 0.19% 0.19% H₂ 0.87% 0.23% CO₂ 8 % 8 % NO 0.17% 0.17% O₂ 0.65% 1.8 % H₂O 10% 10 % N₂ Remainder Remainder [0020] The rich gas and lean gas of the durability test above were switched every 5 seconds, it repeated at 900 degrees C for 30 minutes, the cycle of 30 minutes was repeated 15 times at 750 degrees C, and the durability test was performed. Catalytic activity was measured by the aforementioned approach also after the durability test. The measurement result of the catalytic activity before a durability test and the test result of the catalytic activity after a durability test are shown in Table 2.

[0021]

[Table 2]

各試験での 50% 済化温度 (C)

No.	初期			耐久後		
	NO	CO	HC	NO	CO	HC
実施例 1	207	204	215	268	274	287
実施例 2	140	150	151	221	218	233
実施例 3	215	217	223	271	266	278
実施例 4	136	132	138	207	227	228
実施例 5	156	141	155	211	227	232
実施例 6	186	158	158	260	225	257
比較例 a	236	227	242	370	332	349
比較例 b	253	245	256	374	288	332
比較例 c	233	225	236	432	365	382
比較例 d	317	306	341	>500	394	393
比較例 e	198	193	208	259	263	276

[0022] In each example, 50% purification temperature is low, and it is high in each example of a comparison so that clearly from the result of Table 1.

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